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XII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON BENZYLDIMETHYLAMINE.

BY C. LORING JACKSON AND JOHN F. WING.

At the beginning of the last academic year we prepared the benzyldimethylamine with the intention of making an extended research on this substance; but as the carrying out of this research has been indefinitely postponed on account of the pressure of other more interesting work, we have thought it proper to publish the results already obtained, consisting of the preparation and properties of the base and some of its salts, for the benefit of any one who may follow us in this line of research, rather than on account of any especial interest in the results themselves.

The benzyldimethylamine has been already obtained by Schotten,* as one of the products of the distillation of the free base derived from the addition product of methylbenzylpiperidine and methyl iodide; but he contented himself with the determination of its presence by the analysis of its chlorplatinate.

Benzyldimethylamine. — To prepare the substance an alcoholic solution of dimethylamine was made by the decomposition of nitrosodimethylaniline, according to the method of Baeyer and Caro,† the gas being passed into absolute alcohol, and this was allowed to stand for some hours with benzylchloride. At the end of this time, the reaction, which was accompanied with evolution of heat, was finished; and after distilling off the alcohol on the water-bath, the product was treated with water, and then with hydrochloric acid, after which it was extracted with ether to remove a slight non-basic impurity. The base was then set free with sodic hydrate, extracted with ether, washed in the ethereal solution, dried with potassic hydrate, and purified by distillation after driving off the ether. The aqueous liquid, from which

* Ber. d. ch. G., 1882, p. 424.

† Ibid., 1874, p. 963.

the base was extracted with ether, contains the excess of dimethylamine, and the chloride of dibenzyltrimethylammonium, the extraction of which will be described later in this paper.

Properties of the Benzyltrimethylamine. — It forms a colorless liquid with a peculiar smell, boiling at $183-184^{\circ}$ * with the column entirely in the vapor and the barometer at 76.53 cm. It is insoluble in water, but mixes freely with alcohol or ether. Two attempts to convert it into a nitroso-compound gave negative results.

The *Chloride* is deliquescent, and forms white radiating crystals.

The *Nitrate* is also deliquescent, so that crystals can be obtained only with difficulty; it forms slender white needles, with many shorter ones crossing them at right angles.

The composition of the base was determined by the analysis of its chlorplatinate and acid ferrocyanide.

Chlorplatinate, $[C_7H_7(CH_3)_2N]_2H_2PtCl_6$. — The salt was prepared by adding chlorplatonic acid to the free base, purified by crystallization from water, dried at 100° , and analyzed.

- I. 0.2288 gr. of the salt left on ignition 0.0656 gr. of platinum.
- II. 0.3320 gr. left 0.0944 gr. of platinum.
- III. 0.3994 gr. left 0.1148 gr. of platinum.
- IV. 0.4244 gr. left 0.1216 gr. of platinum.

	Calculated for $[C_7H_7(CH_3)_2N]_2H_2PtCl_6$.	I.	II.	III.	IV.
Platinum	28.63	28.67	28.43	28.74	28.65

Properties. — The appearance of the substance varied a great deal, according to the conditions under which the crystals were obtained; thus we have observed it in thick orange prisms, in long yellow needles, or in pointed crystals shaped like a spear-head.† It is slightly soluble in water, and in alcohol. Water is the best solvent for it, good crystals being easily obtained from the aqueous solution.

Ferrocyanide, $(C_7H_7(CH_3)_2N)_2H_4Fe(CN)_6$. — This substance was obtained as a white precipitate, when a solution of potassic ferrocyanide was added to a slightly acid solution of the chloride. It contains no water of crystallization, and its composition was determined by the following analyses.

* This determination of the boiling point was made with too small a quantity of the substance, and must be considered as merely approximate. If we had continued the research, we should have repeated it on a more satisfactory scale.

† The identity of the substance in all these forms was proved by analyses.

I. 0.5224 gr. of the salt dried in vacuo gave on ignition 0.0852 gr. of ferric oxide.

II. 0.3714 gr. gave 0.0612 gr. of ferric oxide.

	Calculated for	Found.	
	$[C_7H_7(CH_3)_2N]_2H_4FeCN.$	I.	II.
Iron	11.53	11.41	11.53

Properties. — It forms white pearly scales, which are very sparingly soluble in water, and on exposure to the air turn slightly green, but the amount of the decomposition thus indicated is so small as to be inappreciable by analysis.

With mercuric chloride the base gave an uninviting viscous product, while with zincic chloride it formed a characteristic double salt, which separated from concentrated solutions as an oil, but soon solidified in good-sized rhombic crystals; an analysis of a not perfectly pure sample of this salt led to the following results.

0.3492 gr. of the salt gave 0.4090 gr. of argentic chloride.

	Calculated for	Found.
	$[C_7H_7(CH_3)_2NHCl]_2ZnCl_2.$	
Chlorine	29.65	28.95

Dibenzyltrimethylammonium Chloride, $(C_7H_7)_2(CH_3)_3NCl$. — This substance was left in the aqueous solution after the benzyldimethylamine had been shaken out with ether, and, when this solution was evaporated to one half its original volume, separated as a yellow oil, which solidified as it cooled. It can be freed partially from the inorganic salts present mechanically, or by solution in chloroform, although chloroform does not remove it from its aqueous solution, and purified by washing with a saturated solution of sodic carbonate, and finally dissolving it out of the inorganic impurities with alcohol or chloroform.

Properties. — It forms white rhombic crystals often in spear-head forms and a centimeter broad, or masses of radiating prisms or needles, but usually separates from its solutions as an oil, which solidifies after standing for some time, more rapidly if touched with a crystal of the substance. It is freely soluble in water, but nearly insoluble in a saturated solution of sodic carbonate, soluble with some difficulty in alcohol, but freely in chloroform, which is the best solvent for it; it is also soluble in ether, benzol, carbonic disulphide, and glacial acetic acid, insoluble in ligroine. When heated, it gives benzylchloride, recognized by its smell and action on the eyes, and a base, which however seems to boil at a higher temperature than the benzyldimethylamine; but the experiment should be repeated on a larger scale. If the

aqueous solution of the chloride is boiled with argentic oxide, it becomes strongly alkaline, but it is necessary to boil for some days in order to convert it completely into the free base.

Dibenzyltrimethylammonic Chloroplatinate, $[(C_7H_7)_2(CH_3)_3N]_2PtCl_6$. — This substance was prepared by adding an alcoholic solution of the chloride to chlorplatinic acid, and purified by recrystallizing from water. Its composition was determined by the following analysis.

0.2012 gr. of the salt gave 0.0454 gr. of platinum.

	Calculated for $[(C_7H_7)_2(CH_3)_3N]_2PtCl_6$.	Found.
Platinum	22.64	22.56

It is nearly insoluble in cold water, but crystallizes from a hot aqueous solution in large shining yellow plates, often a centimeter in length, or in feather-like forms.